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## XI. "Note on the Oxidation and Disoxidation effected by the Peroxide of Hydrogen." By B. C. BRODIE, F.R.S., Professor of Chemistry in the University of Oxford. Received September 9, 1861.

In a former communication* I laid before the Society a detailed investigation as to the remarkable disoxidation of certain metallic oxides (of which the decomposition of the oxide of silver may be regarded as typical) by the peroxide of hydrogen. I suggested that this decomposition was of a simple and normal chemical character; that the element oxygen was formed according to a molecular law identical with that according to which compound substances are formed; and that the mutual decomposition of the two oxides was determined by the synthesis of the particles of oxygen in opposite polar conditions, according to the equation

$$Ag_2 O + H_2 O_2 = Ag_2 + H_2 O + O_2.$$

After an interval of nearly ten years, this explanation, together with various facts bearing upon the theory of this action, and which were given for the first time in the paper alluded to, have been reproduced as original discoveries by Schönbein, Professor of Chemistry at Basle†.

The reaction does not, however, present itself under this simple form. The amount of oxygen lost by the oxide of silver is a variable quantity, comprised between the extreme limits of the catalytic action in which the reduction is zero, and the normal chemical action as expressed in the above equation. The reason for this variation is to be sought in the disturbing influence of the metal formed during the decomposition.

It is my intention shortly to communicate to the Society a prosecution of the above inquiry, in which I investigate the decomposition by the peroxide of hydrogen of certain oxygenated substances contained in solution, where the perturbing causes which affect the decomposition of the solid oxides and conceal the simplicity of the reaction, do not exist.

The methods by which the following results have been obtained will hereafter be given in detail. I confine myself to a brief *résume* of the conclusions.

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* Phil. Trans. ii. 1850, 759.

† Phil. Mag. [4] xvi. 178.

(1) * When an acid solution of permanganic acid is decomposed by peroxide of hydrogen, the decomposition is in an invariable atomic proportion, according to the equation

$$Mn_4 O_7 + 5 H_2 O_2 = 2 Mn_2 O + 5 H_2 O + 5 O_2.$$

(2) An alkaline solution of ferricyanide of potassium is reduced by the peroxide of barium to ferrocyanide, with the evolution of two atoms of oxygen, thus

$$2 K_3 Fe_2 Cy_6 + 2 KHO + Ba_2 O_2 = 2 K_4 Fe_2 Cy_6 + 2 Ba HO + O_2.$$

(3) An alkaline solution of hypochlorite of barium is reduced by the peroxide of barium, according to the equation

$$Ba Cl O + Ba_2 O_2 + H_2 O = Ba Cl + 2 Ba HO + O_2.$$

A similar change takes place, as might be anticipated, with an aqueous solution of chlorine in the acid solution of peroxide of barium, but more slowly. I have elsewhere shown that the action of iodine is expressed by the equation

$$I_2 + Ba_2 O_2 = 2 Ba I + O_2.$$

(4) The decomposition of chromic acid is of special interest. In this case there are two distinct reactions, the first of which takes place when chromic acid is in excess, according to the equation

$$2 Cr_2 O_3 + 3 H_2 O_2 = Cr_4 O_3 + 3 H_2 O + 3 O_2;$$

the second, which occurs when a large excess of peroxide of hydrogen is present, and in which the peroxide of hydrogen loses exactly double the amount of oxygen lost by the chromic acid, so that the final result is expressed by the equation

$$2 Cr_2 O_3 + 6 H_2 O_2 = Cr_4 O_3 + 6 H_2 O + O_9.$$

In the interval between these reactions the ratio of the loss of oxygen from the peroxide to the loss from the chromic acid varies between the limits 1 and 2 according to a definite law, being proportional to the ratio of the masses of the substances employed. I am able to show, by direct experiment, that the reaction between the extreme limits is the sum of two distinct and simple atomic decompositions.

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* This reaction has, I find, been published by Aschoff (see Repertoire de Chimie Pure, August 1861, page 296). It was last year made the subject of a communication by me to the British Association, "On the Quantitative Estimation of the Peroxide of Hydrogen."

The alkaline peroxides which produce these peculiar effects of reduction, under other conditions act as powerful oxidizing agents; thus an acid solution of ferrocyanide of potassium is oxidized by peroxide of hydrogen to ferricyanide. Hydrated protoxide of manganese is oxidized by peroxide of barium to the condition of peroxide of manganese. A concentrated solution of hydrochloric acid evolves chlorine from peroxide of barium.

This last reaction I have made the subject of a special investigation, with the view of determining the conditions under which the two reactions,

$$4\,HCl + Ba_2O_2 = 2\,BaCl + 2\,H_2O + Cl_2,$$

and

$$2\,HCl + Ba_2O_2 = 2\,BaCl + H_2O_2,$$

respectively take place; and I find that when a solution of hydrochloric acid is boiled with peroxide of barium, if the solution be concentrated, chlorine, if the solution be dilute, oxygen, exclusively is evolved; and that for each intermediate degree of dilution chlorine and oxygen together are evolved in a constant ratio.

It is thus seen that those differences in the behaviour of the different classes of peroxides, from which an imaginary distinction has been drawn between the oxygen respectively contained in them as positive or negative, are not fundamental and characteristic differences. The oxygen in the peroxide of barium is the same as that in the peroxide of manganese, according to the only test of identity which we can apply, for we can produce with it the same effects. Nor are the peculiarities in the reactions of the oxygen of the alkaline peroxides of such a nature as to need any special hypothesis to account for them; for in no case are the combining properties of the particles of matter, like their atomic weights, constant for each chemical substance, but they are variable properties, depending on the physical conditions in which the particles are placed, and the chemical substances with which they are associated.